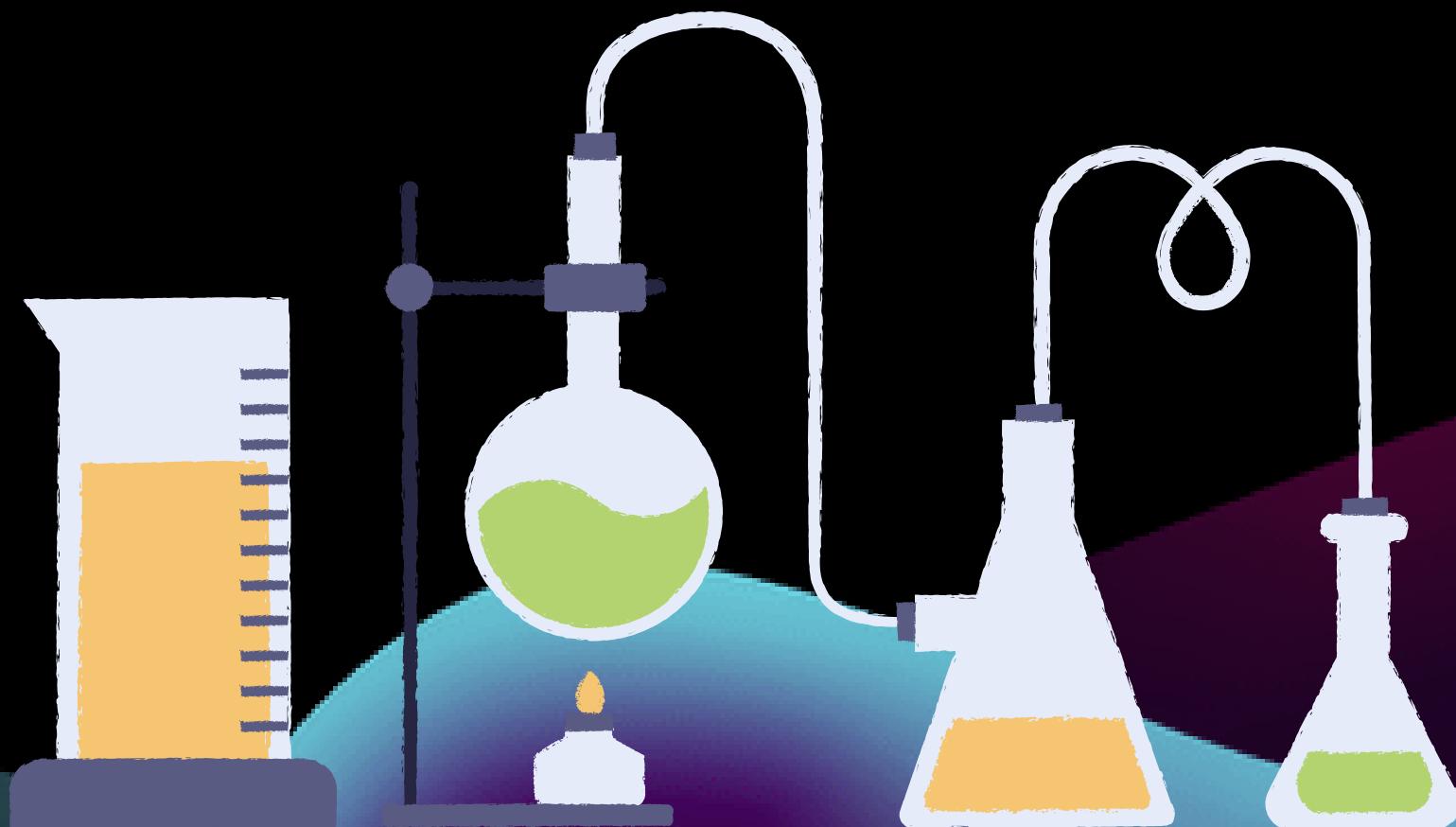


# Modeling solubility in supercritical fluids via the virial equation of state

PRESENTED BY



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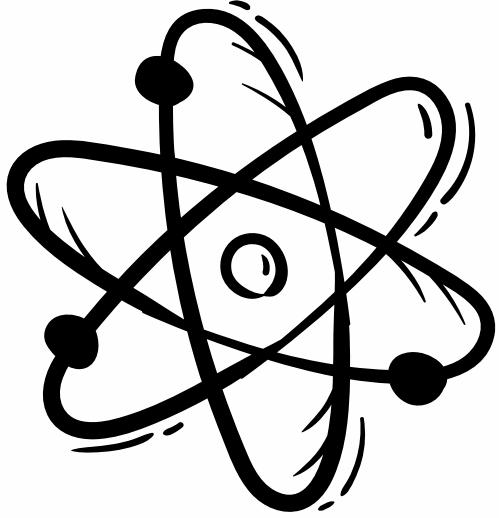
# AIM

The primary aim of this study is to initiate with a straightforward exercise, applying the Virial Equation of State (VEOS) to the van der Waals and Soave–Redlich–Kwong equations of state.

- The specific objective is to characterize the convergence behavior of the virial series.
- Following this initial exercise, the focus shifts towards investigating the solubility of hexane in carbon dioxide (CO<sub>2</sub>).
- Realistic molecular models for hexane and CO<sub>2</sub> are employed to calculate the mixture virial coefficients.
- Moving forward, the presentation and analysis of properties derived from the resulting VEOS are discussed.
- Finally, the study concludes by summarizing findings and insights gained from this exploration.



# INTRODUCTION



## **Supercritical State**

A critical point is a specific temperature and pressure at which a substance has properties of both a liquid and a gas, exhibiting characteristics of both phases.

When a substance is heated and pressurized past its critical point, it enters a state known as the supercritical state. In this state, the distinction between liquid and gas phases disappears.

Till now many modeling approaches have been examined to quantify and predict the behavior of supercritical fluids and their mixtures. Joslin et al. presented a brief but comprehensive survey of these methods, summarizing the strengths and weakness of each. Such techniques include :-

- Empirical Engineering Models (e.g. cubic equations of state),
- Molecular simulations.
- Integral Equation methods,
- Lattice models,
- Perturbation theory.

# VIRIAL EQUATION OF STATE (VEOS)

Joslin et al. considered in detail the capabilities of another type of approach, one modeling the supercritical phase with a virial equation of state (VEOS), using parameters determined directly from a molecular model. **The VEOS for a binary mixture of species 1 and 2 gives the pressure P as a series in the molar density (rho) !**

$$\frac{P}{RT} = \rho + \sum_{n=2}^{\infty} \left( \sum_{i=0, j=n-i}^n \frac{n!}{i!j!} B_{ij}(T) y_1^i y_2^j \right) \rho^n$$

where **T is the temperature** and **R is the gas constant**. The **B<sub>ij</sub>** is the mixture virial coefficient corresponding to i molecules of species 1 and j molecules of species 2. It depends upon the temperature but are independent of mole fractions y. We refer to the expression contained in the parentheses as B<sub>n</sub>, analogous to the VEOS for a pure fluid. We use **VEOS<sub>n</sub>** to represent the VEOS truncated after the n<sup>th</sup>-order term.

The use of VEOS for supercritical fluid phenomena has been limited due to difficulties in determining virial coefficients without experimental data. This constraint reduces the predictive power of the method as it relies on empirical values.

VEOS excels in its ability to rigorously define parameters based on molecular interactions. This capability is beneficial because it allows for a more accurate and detailed representation of the underlying molecular principles in the thermodynamic model



# MODELS AND METHODS



**Considering that species 2 is infinitely dilute in solvent 1 ( $x_1=1, x_2=0$ ). In this model, the solute fugacity coefficient is:**

$$\ln \phi_2 = \ln \left( \frac{1}{1 - b_1 \rho} \right) + \frac{b_2 \rho}{1 - b_1 \rho} - \frac{2 \rho \sqrt{a_1 a_2}}{RT} - \ln Z \quad (4)$$

**The infinite-dilution low-density expansion of the fugacity coefficient is**

$$\ln \phi_2^v = \sum_{n=1}^{\infty} \frac{n+1}{n} B_{n1} \rho^n - \ln Z \quad (5)$$

**where  $B_{ij}$  is the mixture virial coefficient corresponding to  $i$  molecules of species 1 and  $j$  molecules of species 2; the  $v$  superscript on  $\phi$  indicates the values as given by the VEOS. Comparison of this series to an expansion of Eq. (4) for  $\rho \rightarrow 0$  gives the mixture virial coefficients in terms of the vdW parameters**

$$B_{11} = \frac{1}{2} (b_1 + b_2) - \frac{\sqrt{a_1 a_2}}{RT}$$

$$B_{n1} = \frac{1}{n+1} (b_1^n + n b_1^{n-1} b_2) \quad n > 1$$

We use the following values of the pure component parameters that match the critical properties of each species with the vdW critical point:  $a_{\text{CO}_2} = 3.658 \text{ bar-(L/mol)}^2$ ,  $b_{\text{CO}_2} = 0.0429 \text{ L/mol}$ ,  $a_{\text{benzene}} = 18.82 \text{ bar-(L/mol)}^2$ ,  $b_{\text{benzene}} = 0.1193 \text{ L/mol}$ ,  $a_{\text{hexane}} = 24.84 \text{ bar-(L/mol)}^2$ , and  $b_{\text{hexane}} = 0.1744 \text{ L/mol}$  [25].

# VEOS estimates of model Van der Waals and Soave-Redlich-Kwong binary mixtures

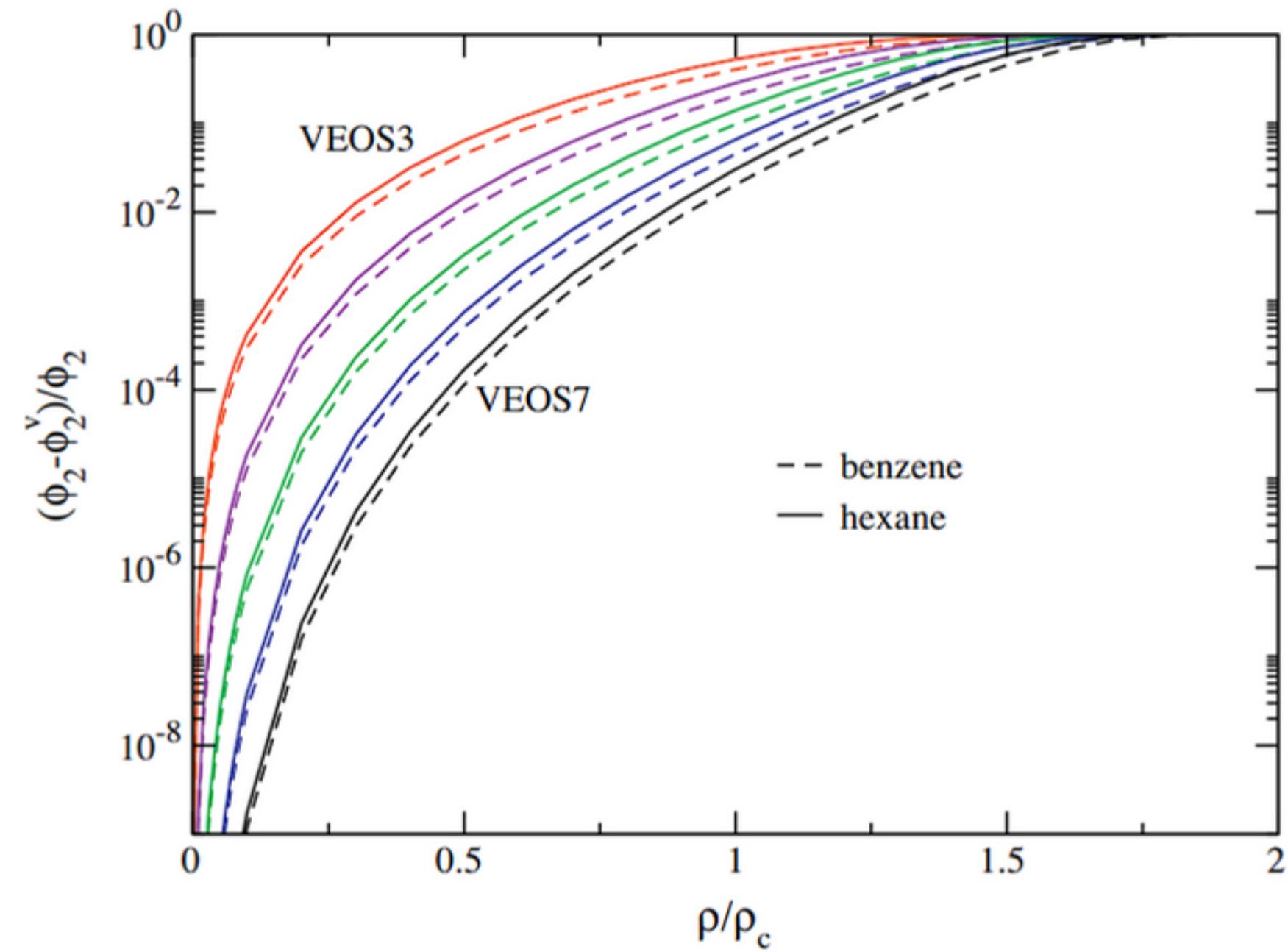
Harvey explored the VEOS's applicability for supercritical solubility, initially examining VEOS3 approximations to various cubic equations of state (including van der Waals and Soave–Redlich–Kwong equations) for carbon dioxide mixed with benzene, naphthalene, or anthracene. With the potential to use higher-order VEOSn, we aim to expand Harvey's analysis by considering formulations up to VEOS7. Specifically, we explore mixtures as defined by the van der Waals equation of state and the more realistic Soave–Redlich–Kwong equation of state, investigating the dissolution of benzene and hexane in carbon dioxide.

We first consider the vdW equation of state

$$Z \equiv \frac{P}{\rho RT} = \frac{1}{1 - b\rho} - \frac{a\rho}{RT} \quad (2)$$

for a binary mixture, with Lorentz–Berthelot mixing rules for the vdW parameters a and b given in terms of the pure component parameters  $a_i$  and  $b_i$

$$a = y_1^2 a_1 + 2y_1 y_2 \sqrt{a_1 a_2} + y_2^2 a_2 \quad b = y_1 b_1 + y_2 b_2 \quad (3)$$



**Fig. 1.** The negative of the relative error in the  $\text{VEOS}_n$  infinite-dilution solute fugacity coefficient for (a) benzene dissolved in  $\text{CO}_2$  and (b) hexane dissolved in  $\text{CO}_2$  as a function of the density reduced by the critical density of  $\text{CO}_2$  at the critical temperature of  $\text{CO}_2$ . The exact behavior is assumed to be given by the vdW equation of state.

In Fig. 1, we plot the fractional error in the  $\text{VEOS}$  fugacity coefficient, given by the ratio of  $\phi_2 - \phi_2^v$  to  $\phi_2^v$ , with respect to reduced density for  $\text{VEOS}3$  through  $\text{VEOS}7$  at the critical temperature of  $\text{CO}_2$ , 304.13 K. As shown by Harvey, the error of  $\phi_2^{\text{VEOS}3}$  for the  $\text{CO}_2$ -benzene mixture is significant (about 40%) at the critical density of  $\text{CO}_2$ , but each subsequent increase in order of the  $\text{VEOS}$  reduces the error at this density by about a factor of two. For  $\text{VEOS}7$ , the error is about 2%. At densities beyond the critical density, the  $\text{VEOS}$  approximation to the vdW EOS becomes increasingly poor and fails completely as  $\rho/\rho_c$  approaches 2. The fractional errors for each hexane  $\text{VEOS}_n$  estimate are slightly worse than the respective benzene  $\text{VEOS}_n$  estimate. One may consider that, with a larger vdW  $b$  value, hexane is larger than benzene, and thus could be solvated by more  $\text{CO}_2$  molecules, making higher-order  $B_{n1}$  coefficients more relevant at a given density.

We next consider VEOS approximations for the same two mixtures as described by the SRK equation of state.

$$Z \equiv \frac{P}{\rho RT} = \frac{1}{1 - b\rho} - \frac{\bar{a}\rho}{RT} \frac{\alpha(T)}{(1 + b\rho)} \quad (7)$$

We employ expressions for the SRK parameters that match the critical properties of each species [24] with the SRK critical point

$$a = \bar{a}\alpha(T)$$

$$\bar{a} = 0.42748 \frac{(RT_c)^2}{P_c}$$

$$\alpha(T) = \left[ 1 + (0.480 + 1.574\omega - 0.176\omega^2) \left( 1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \quad (8)$$

$$b = 0.08664 \frac{RT_c}{P_c}$$

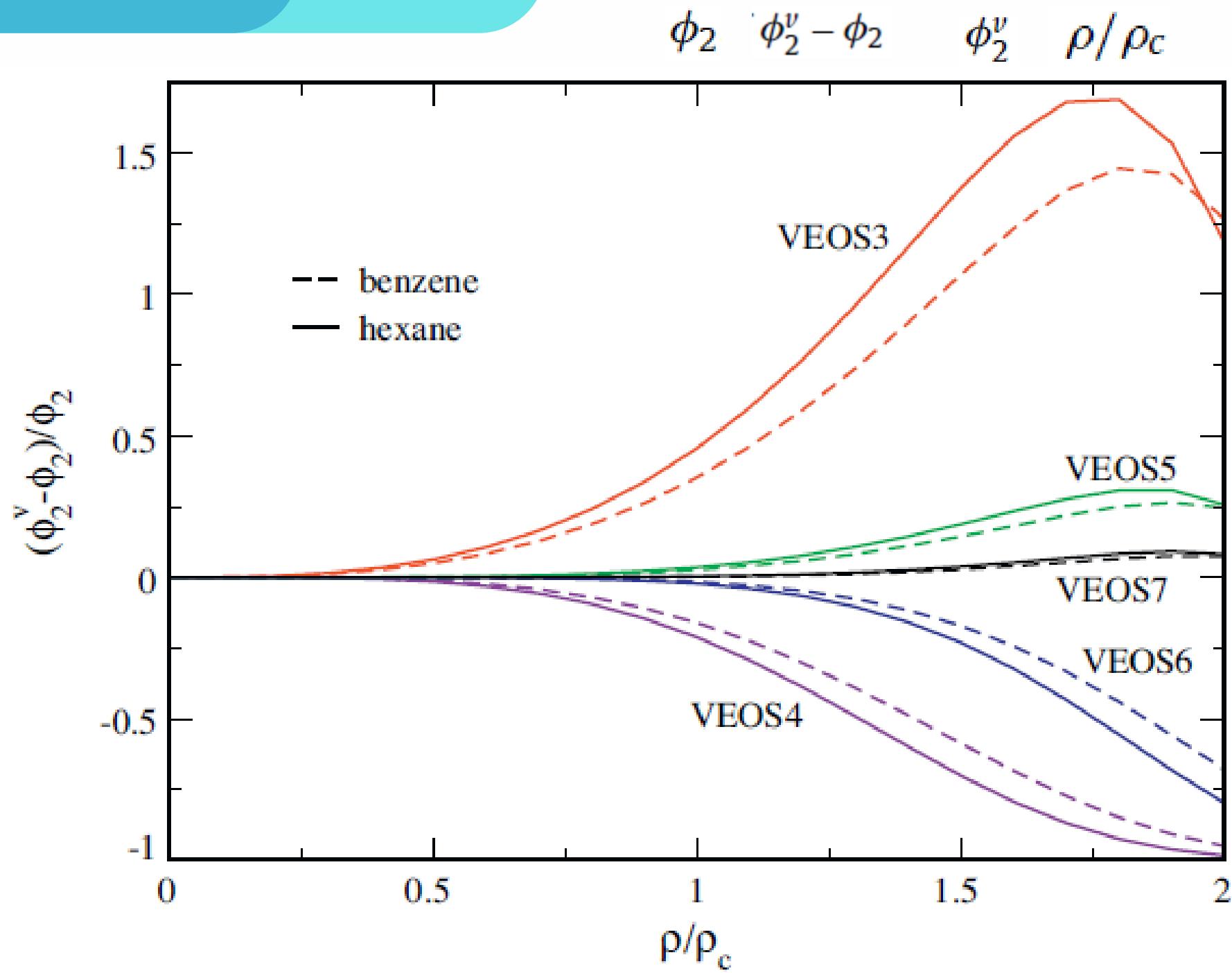
We use the following values of the pure-component properties and parameters:  $T_{c,\text{CO}_2} = 304.1$  K,  $P_{c,\text{CO}_2} = 7380$  kPa,  $\omega_{\text{CO}_2} = 0.239$ ,  $T_{c,\text{benzene}} = 562.1$  K,  $P_{c,\text{benzene}} = 4890$  kPa,  $\omega_{\text{benzene}} = 0.212$ ,  $T_{c,\text{hexane}} = 507.5$  K, and  $P_{c,\text{hexane}} = 3010$  kPa,  $\omega_{\text{hexane}} = 0.299$  [24]. The resulting values of the parameter  $b$  are notably smaller for each species than for the vdW EOS:  $b_{\text{CO}_2} = 0.0297$  L/mol,  $b_{\text{benzene}} = 0.0828$  L/mol, and  $b_{\text{hexane}} = 0.1215$  L/mol.

Using the same Lorentz–Berthelot combining rules we did for vdW parameters (Eq. (3)), the fugacity coefficient,  $\phi_2$  is [24]

$$\begin{aligned} \ln \phi_2 = & \ln \left( \frac{1}{1 - b_1\rho} \right) + \frac{b_2\rho}{1 - b_1\rho} - \frac{2\sqrt{a_1a_2}}{RTb_1} \ln(1 + b_1\rho) \\ & + \frac{a_1b_2}{RTb_1^2} \left[ \ln(1 + b_1\rho) - \frac{b_1\rho}{1 + b_1\rho} \right] - \ln Z \end{aligned} \quad (9)$$

As before, we match terms from the density expansion of Eq. (9) with terms in Eq. (5) to determine expressions for virial coefficients in the limit of infinite dilution in terms of the SRK parameters

$$\begin{aligned} B_{n1} = & \frac{1}{n+1} \left[ b_1^n + nb_1^{n-1}b_2 \right] + (-1)^n \frac{b_1^{n-2}}{(n+1)RT} \\ & \times \left[ 2\sqrt{a_1a_2}b_1 + (n-1)a_1b_2 \right] \quad n \geq 1 \end{aligned} \quad (10)$$



**Fig. 2.** Relative error in the VEOS $n$  infinite-dilution solute fugacity coefficient for (a) benzene dissolved in CO<sub>2</sub> and (b) hexane dissolved in CO<sub>2</sub> as a function of the density reduced by the critical density of CO<sub>2</sub> at the critical temperature of CO<sub>2</sub>. The exact behavior is assumed to be given by the SRK equation of state.

In Fig. 2, we plot the fractional error in the VEOS fugacity coefficient, given by the ratio of  $\phi_2^v - \phi_2$  to  $\phi_2$ , with respect to reduced density for VEOS<sub>3</sub> through VEOS<sub>7</sub> at the critical temperature of CO<sub>2</sub>. Unlike the VEOS as applied to the vdW EOS,  $\phi_2^v$  is sometimes too large and sometimes too small, but still converges to the correct result with enough terms. The error of  $\phi_2^{\text{VEOS}3}$  for the mixtures is about 35% (similar to the vdW EOS) at the critical density of CO<sub>2</sub>, but additional terms of the VEOS reduce the error more quickly than when applied to the vdW EOS, so that the error in VEOS<sub>7</sub> is only 0.24%. This could be in part the result of the smaller  $b$  values and the characterization of molecular asymmetry through the acentric factor  $\omega$ . The VEOS approximation to the SRK EOS continues working well up to very high density, with only 7% error in VEOS<sub>7</sub> at  $\rho/\rho_c = 2$ .

# Molecular models

Our study utilizes molecular models previously investigated by Cui et al. The models were initially assessed via Gibbs-ensemble Monte Carlo (GEMC) simulations for CO<sub>2</sub>-hexane systems. Cui et al. aimed to evaluate these models' capacity to describe hexane solubility in supercritical CO<sub>2</sub>, comparing the simulations to experimental data.

In our analysis, we aim to assess the VEOS's ability to quantitatively depict the behavior of these models and their efficacy in representing the experimental system.

The model for hexane is based on the alkane potential proposed by Siepmann et al., a flexible united-atom model that includes bond bending and torsion but doesn't permit bond stretching. Carbon dioxide is modeled using the EPM2 model by Harris and Yung, a rigid linear three-site model incorporating point charges to simulate electrostatics.

While Cui et al. applied potential truncation with corrections for neglected long-range interactions in their simulations, our approach differs. We conduct calculations with an infinite simulation volume rather than periodic boundary conditions, potentially influencing the model's behavior. This variation could potentially impact our results compared to Cui et al.'s GEMC approach, although we haven't quantitatively examined this difference in our models' application.

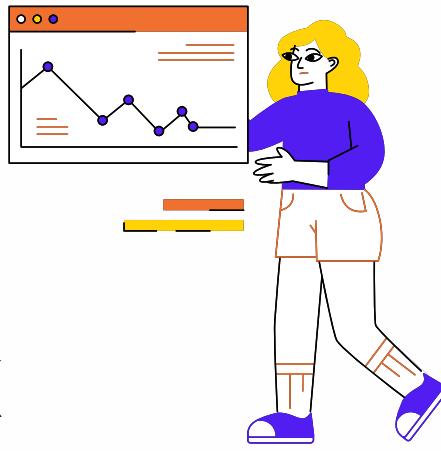
# Evaluation of virial coefficients for molecular models

The virial coefficients for a pure fluid are given in terms of cluster integrals involving interactions among n molecules for the coefficient  $B_n$ . The classical second virial coefficient is

$$B_2(T) = -\frac{1}{2N_A V \Omega^2} \iint f_{12} e^{-\beta U_1} e^{-\beta U_2} dr_1 dr_2 d\omega_1 d\omega_2$$

where  $\beta = 1/kT$  with k the Boltzmann constant;  $N_A$  is Avogadro's number. The integral is performed over all positions  $r_1$  and  $r_2$  in a volume  $V$ , which is taken to be infinite. In practice we effect the division by  $V$  by holding the position of molecule 1 fixed. The symbols  $\omega_1$  and  $\omega_2$  represent all orientational and internal (conformation) coordinates of molecules 1 and 2, respectively, and  $U_i(\omega_i)$  is the intramolecular energy for molecule i. The integrals over  $\omega$  are normalized by dividing by  $\Omega \equiv \int e^{-\beta U(\omega)} d\omega$ . Also,  $f_{12} = \exp(-\beta u(r_1, r_2, \omega_1, \omega_2)) - 1$  is the Mayer function, where  $u$  is the total intermolecular energy between molecules 1 and 2. The mixture coefficients  $B_{20}$ ,  $B_{11}$ , and  $B_{02}$  are all given by this integral, differing only in the choice of the species of the two molecules that are integrated upon. Expressions for higher-order coefficients  $B_n$  involve sums of integrals over n molecules, with the number of integrals growing rapidly with n.

# Results



We report components of the mixture coefficients  $B_2$ ,  $B_3$ , and  $B_4$  at 353.15 K

**Table 1**

Mixture virial coefficients for the model CO<sub>2</sub>-hexane system.  $B_{ij}$  is the coefficient for  $i$  molecules of CO<sub>2</sub> and  $j$  molecules of hexane. Numbers in parenthesis indicate 67% confidence limits in the last digit(s) of the reported value.

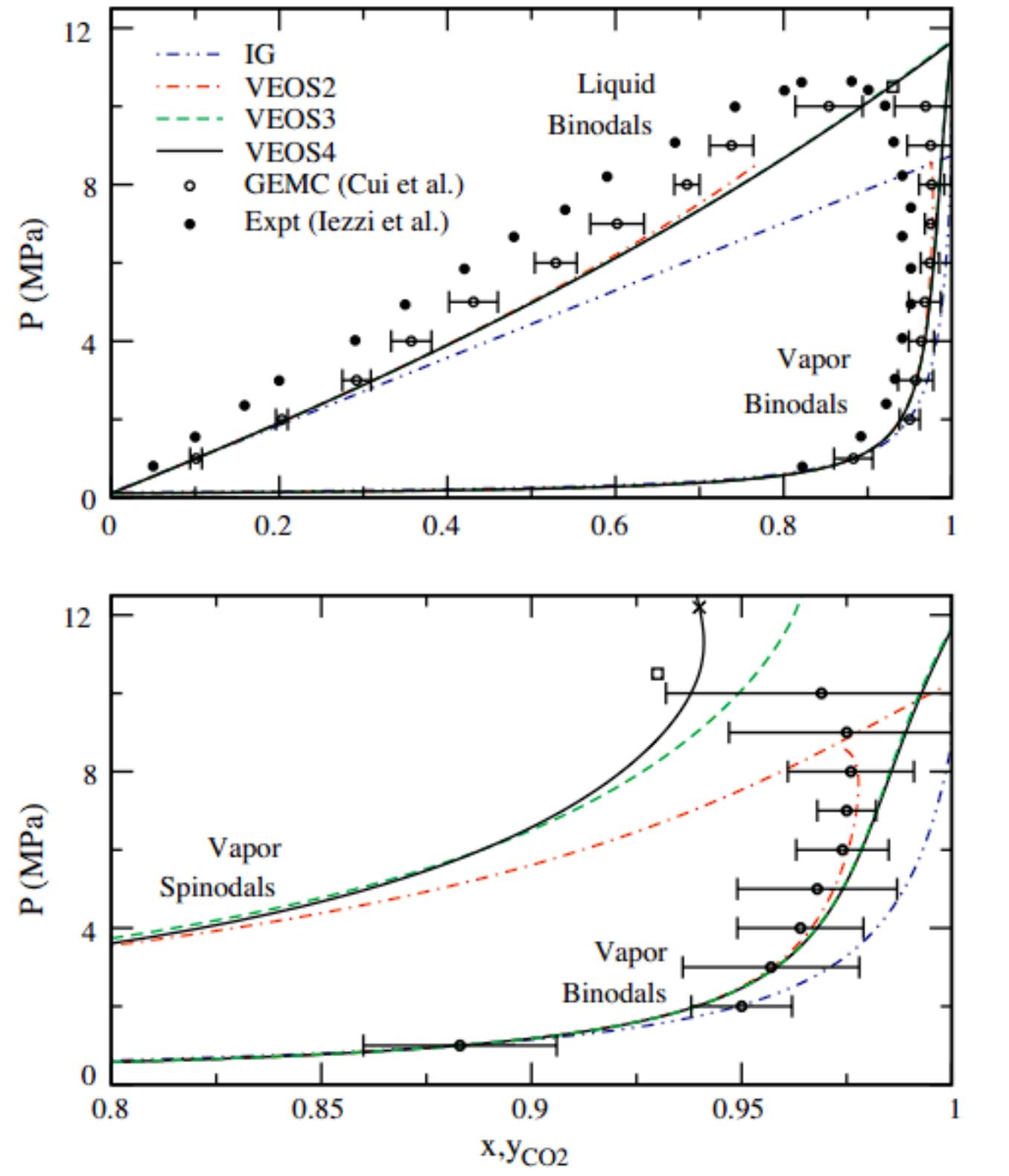
$B_2$ components (L/mol)	$B_3$ components (L/mol) <sup>2</sup>	$B_4$ components (L/mol) <sup>3</sup>
$B_{20}$ -0.071473(2)	$B_{30}$ 0.0024603(5)	$B_{40}$ 0.0000382(2)
$B_{11}$ -0.258526(12)	$B_{21}$ 0.008623(8)	$B_{31}$ 0.000222(8)
$B_{02}$ -1.19608(12)	$B_{12}$ 0.03373(7)	$B_{22}$ 0.00144(5)
	$B_{03}$ -0.1554(4)	$B_{13}$ 0.0111(5)
		$B_{04}$ -0.514(4)

We use these coefficients to obtain VEOS estimates of the chemical potentials  $\mu_i$  of carbon dioxide and hexane in the vapor phase. From these  $\mu_i$ , one can determine the range of conditions for which the vapor mixture is stable with respect to fluctuations in the number of molecules of species  $i$ ,  $N_i$  :

$$\left( \frac{\partial \mu_1}{\partial N_1} \right)_{T,P,N_2} > 0$$

which can be rewritten into a form more suitable for the VEOS. The spinodal is the locus of points for which Eq. (12) is satisfied as an equality. Barring numerical problems or inadequacies in the model, the spinodal typically ends at a stable critical point where the following condition also holds

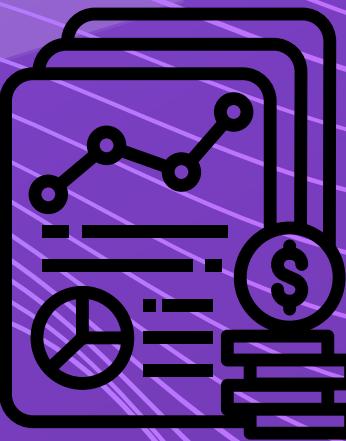
$$\left( \frac{\partial^2 \mu_1}{\partial N_1^2} \right)_{T,P,N_2} = 0$$



**Fig. 3.** Pressure-composition diagram for the system  $\text{CO}_2$ -hexane at 353.15 K. (Top) VEOS $n$  estimates of both vapor and liquid coexistence curves are shown. (Bottom) Lines show VEOS $n$  estimates of the vapor spinodals and VEOS $n$ /ideal-mixture estimates of the vapor-liquid coexistence curve. Unfilled circles are GEMC simulation data [27] for the vapor-liquid coexistence curve, and filled circles are experimental data [30].

The VEOS2-4 estimates of the spinodal line for the  $\text{CO}_2$ -hexane model system at 353.15 K are depicted in the lower section of Fig. 3. The spinodal line is contrasted against the vapor branch of the coexistence data determined by Cui et al. using Gibbs-ensemble Monte Carlo for the same system, along with experimental measurements. The VEOS-derived spinodal aligns well with the available data, particularly the critical point, estimated at 353.15 K and indicated by a square at a pressure of roughly 10.5 bar. However, the VEOS3 and VEOS4 spinodal lines do not fulfill the critical point criterion. While the VEOS2 spinodal demonstrates accuracy at lower pressures, deviations occur as pressure increases. Attempts to locate the critical point using the VEOS confront the model's limitations in the critical region, where classical models fail to describe behavior accurately without special considerations. Regarding the solubility of hexane in  $\text{CO}_2$ , the present study primarily models the  $\text{CO}_2$ -rich phase due to the supercritical nature of the system. The hexane-rich phase is treated as an ideal solution. The estimated binodal curves utilizing VEOS2-4 and the ideal gas law for the  $\text{CO}_2$ -rich phase are presented. The ideal gas law underpredicts hexane solubility, while VEOS2 offers a significantly improved quantitative description. VEOS3 extends this description further at higher pressures, but unphysical behavior is observed as the ideal-solution model is used beyond its parameterized region. Despite VEOS convergence for vapor conditions, the model's inability to fully capture the liquid phase's behavior affects the predictions of liquid binodals. The discrepancy in hexane solubility, particularly at high pressures, indicates the model's limitations in capturing the full behavior of the liquid phase.

# CONCLUSION



- The use of the virial equation of state (VEOS) to describe supercritical fluid behaviors is a promising approach, particularly when considering molecular parameters derived from Monte Carlo simulations or ab initio chemistry calculations. The applications displayed in this context show significant promise. VEOS<sub>3</sub> properties exhibit convergence at most conditions but struggle at very high pressures near the critical point. The derived vapor-phase binodal agrees well with experiment up to around 8 MPa, indicating that the model hexane shows lower solubility in supercritical CO<sub>2</sub> than observed.
- However, limitations arise in modeling the subcritical phase, employing a basic ideal-solution treatment. Yet, in practical applications, better approaches may exist for modeling the subcritical phase, especially in scenarios involving solid dissolution in supercritical fluids.
- In this study, the VEOS alone doesn't adequately represent the critical region of the mixture. Nonetheless, the spinodal is depicted well, offering a near-miss critical point estimation, albeit not meeting the true criteria of criticality. Future improvements in VEOS modeling, possibly through approaches merging classical and non-classical critical behaviors, could enhance its accuracy in providing information about the critical region.

Thank  
you

